

SUPPRESSION OF REACTIVITY CHANGES IN Poly bd® R-45M RESIN

Harry R. Minney and John R. Murphy
ARCO Chemical Company
A Division of Atlantic Richfield Company
Newtown Square, Pennsylvania

ABSTRACT

Poly bd R-45M resin, a hydroxyl terminated homopolymer of 1,3-butadiene, is a primary component in the binder for many solid propellant systems. The aging characteristics of this resin are such that its rate of reactivity with an isocyanate may increase during storage for prolonged time periods at ambient temperatures. As a result, the pot lives of propellant mixtures prepared from the same lot of Poly bd R-45M resin may differ significantly over a period of months. Under certain processing conditions, this reactivity difference may pose problems for the formulator. The addition of triphenylphosphine to the Poly bd R-45M resin has been found to prevent these reactivity changes.

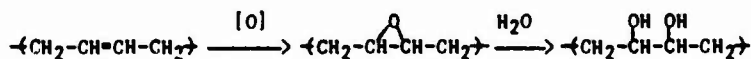
INTRODUCTION

Poly bd R-45M resin, a hydroxyl terminated homopolymer of 1,3-butadiene, is widely utilized in the aerospace industry as a major component in the binder of solid propellant systems. This resin has many desirable properties, including low temperature flexibility, low viscosity, excellent stress and strain characteristics, high solids loading capability, low cost, and low signature of the finished rocket motor. However, the aging characteristics of the resin are such that its rate of reactivity with isocyanates in propellant formulations may increase during storage for prolonged periods at ambient temperatures. As a result, the pot lives of propellant mixtures prepared from the same lot of Poly bd R-45M resin may differ significantly over a period of months. This difference in reactivity can pose a problem for the formulator, who under certain circumstances may continually have to make alterations in the formulating process to compensate for the reactivity increase.

DISCUSSION

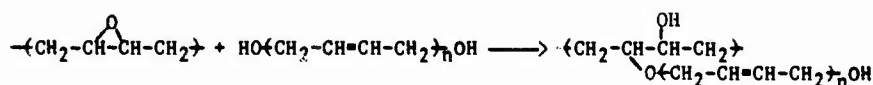
Several hypotheses have been proposed to explain this aging process associated with Poly bd R-45M resin. All of these hypotheses involve either mechanisms which increase molecular weight and/or functionality or catalyze the urethane formation reaction. Increases in molecular weight/functionality might be caused by reaction of trace epoxide groups in the resin or by oxidative degradation of the resin. The presence of metals or acids would catalyze the reaction of Poly bd R-45M resin and isocyanates.

Since Poly bd R-45M resin is a homopolymer of 1,3-butadiene, each repeating unit contains a double bond. These points of unsaturation are susceptible to gradual oxidation either by peroxides or by atmospheric oxygen to form epoxides. These epoxides could potentially react with any water present to produce glycols (Scheme 1). Such an increase in functionality would result in increased crosslinking of the polymer and consequently in shorter pot life.



Scheme 1.

Another mechanism involving epoxides which would increase functionality and molecular weight is the intermolecular addition of a hydroxyl group to an epoxide (Scheme 2). However, experiments indicate that epoxide content remains constant upon aging Poly bd R-45M resin. Thus, a sample of the resin, having an initial gel time of 115 minutes and epoxide content of 0.053%, after aging for 4 months at 135°F gave a gel time of 69 minutes and an epoxide content of 0.057%. Storage of the resin under nitrogen also did not prevent reactivity increase (75 minutes) or affect epoxide content (0.055%). Therefore, it is unlikely that this mechanism is operant.



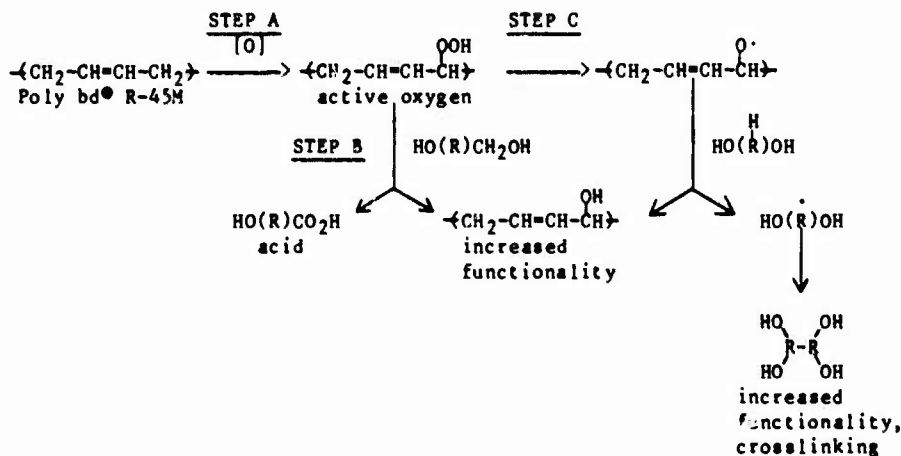
Scheme 2.

The catalytic effect of certain metals on urethane formation from polyols and isocyanates is well known.¹ Increasing reactivity with age might occur via solubilization of metals from storage containers by the Poly bd R-45M resin. This possibility is unlikely, as no difference in metal content was found upon aging. Storage in glass containers failed to prevent reactivity changes. A recent patent² describes the effect of metals on the pot life of solid propellant binder systems and teaches chelation as a method to restore these systems to their original pot life. The addition of chelating agents, including one of those mentioned in the patent, to Poly bd R-45M resin did not restore its original reactivity in whole or in part.

The presence of acidic species can have a marked effect on the reaction rate of Poly bd R-45M resin and isocyanates. For example, as shown in Fig. 1, small amounts of acetic acid, when added to the resin, greatly increase reactivity. Aging experiments were run that showed an increase in acid number from 0.091 meq KOH/g to 0.15 meq KOH/g after 4 months at 135°F. Furthermore, the addition of N-cyclohexyl-N'-phenyl-p-phenylenediamine, a weak organic base which is widely used as a rubber antioxidant, was found to partially restore aged Poly bd R-45M resin to its original reactivity. Also, it significantly slowed, but did not stop, the aging process. Thus, it appears that acid formation plays a role in the aging process.

A third hypothesis proposes that active oxygen species (peroxides, hydroperoxides, etc.) present in the Poly bd R-45M resin decompose over time, causing changes in the structure of the resin. Decomposition of these active oxygen species could cause crosslinking and increased functionality. During aging experiments active oxygen levels decreased from 0.034% (as H₂O₂) to less than 0.007% after 4 months at 135°F. The addition of phosphites to Poly bd R-45M resin reduced active oxygen from 0.034% to an undetectable level after 1 day at 135°F. However, this did not prevent reactivity increase upon subsequent aging. The mere presence (or absence) of active oxygen apparently does not affect reactivity per se, but the above experiments indicate that their degradation may affect the aging process.

Since the experimental evidence pointed to both acid catalysis and oxidative degradation as possible causes of reactivity increase upon aging, a hybrid model was developed.³ The decomposition of active oxygen leads to formation of acidic species and other deleterious chemical changes, such as increased functionality and/or crosslinking of the Poly bd R-45M resin (Scheme 3).



Scheme 3.

Testing of this hypothesis led to the search for a single stabilizer which was weakly basic and also prevented oxidation. Triphenylphosphine (TPP) was selected because of its facile reaction with peroxides⁴⁻⁵ and also because of its basicity.⁶

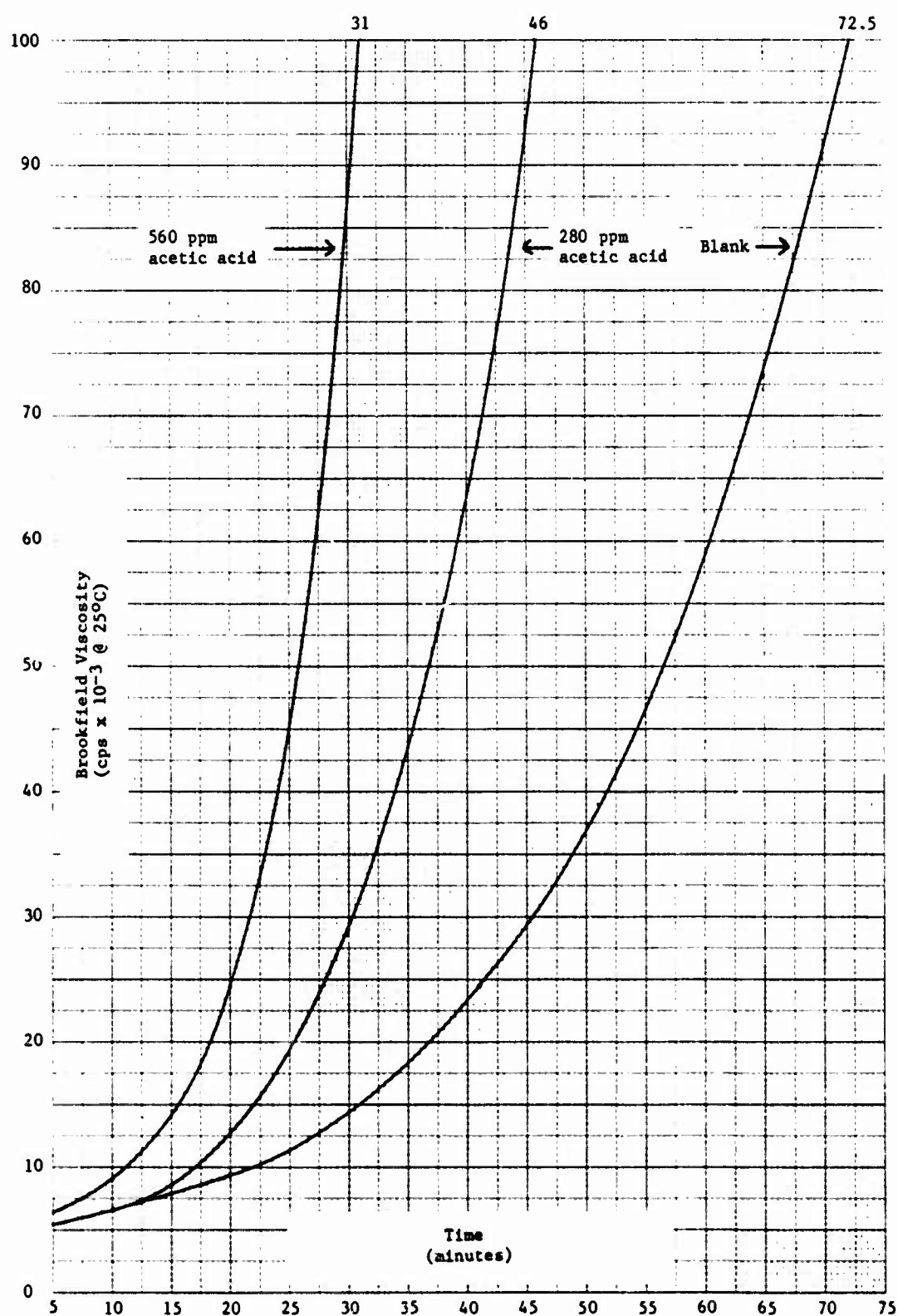


Figure 1.
Effect of Added Acetic Acid on Gel Time

RESULTS

Solutions of stabilizers in Poly bd R-45M resin were prepared and stored in an air-circulating oven at 135°F to accelerate the aging process. No attempt was made to exclude air from the samples, except as noted. All solutions contained 1% by weight of stabilizer.

A gel time test was devised to measure relative reactivity. The viscosity of a mixture of the Poly bd R-45M resin solution and Isonate 143L, a carbodiimide-modified diphenylmethane diisocyanate, at a 1.05 NCO/OH ratio is measured at 25°C. The time required for the reaction mixture to reach a viscosity of 100,000 cps is arbitrarily defined as the gel time and is a measure of the reactivity of the aged resin.

The results using a variety of stabilizer/Poly bd R-45M resin solutions are presented in Table I. The 2,2'-methylenebis-(4-methyl-6-*t*-butylphenol) (AO 2246) is the standard antioxidant added to inhibited grades of Poly bd R-45M resin. The AO 2246 was found to be ineffective in the prevention of reactivity change, although viscosity did remain constant. Initially, the rate of reactivity change was slowed by the AO 2246 when compared to the blank, but by the end of the aging period their gel times were comparable. The AO 2246 is a free radical scavenger⁷ and traps the HO(R)OH formed from decomposition of active oxygen species, preventing crosslinking of the resin (Scheme 3; step C). Hence, no increase in viscosity occurs. However, the AO 2246 apparently prevents neither acid formation nor increased functionality arising from the decomposition of native active oxygen species.

Phenyl didecyl phosphite (PDP), while quickly reducing active oxygen levels to near zero, was totally ineffective at preventing reactivity change and viscosity increase. A combination of AO 2246 and PDP slowed the rate of reactivity change considerably when compared to PDP alone, but again large increases in viscosity occurred. This increase may be a result of the transesterification of the phosphite ester with the Poly bd R-45M resin, since the presence of AO 2246 did not prevent the increase in viscosity.

As mentioned previously, the addition of *N*-cyclohexyl-*N'*-phenyl-*p*-phenylenediamine initially resulted in a reactivity decrease, probably due to its basicity (Scheme 3; step B). Upon aging, only a small increase in reactivity occurred and no increase in viscosity was observed. The *N*-cyclohexyl-*N'*-phenyl-*p*-phenylenediamine evidently also acts to prevent the formation of new active oxygen species (Scheme 3; step A) in the Poly bd R-45M resin, eliminating for the most part an increase in functionality and crosslinking.

Triphenylphosphine (TPP) also initially results in a reactivity decrease. Furthermore, TPP totally prevents reactivity changes upon aging of TPP/Poly bd R-45M resin solutions. Like *N*-cyclohexyl-*N'*-phenyl-*p*-phenylenediamine, TPP partially restores the resin to its original reactivity by acting as an acid scavenger (Scheme 3; step B). According to the hybrid hypothesis, however, complete restoration of reactivity cannot be achieved, as irreversible functionality increase and crosslinking have already occurred (Scheme 3; step C). Only the reactivity increase caused by acid catalysis can be overcome once aging has occurred. TPP apparently also prevents formation of new active oxygen species, obviating the possibility of oxidative degradation and concomitant reactivity increase.

A further advantage of TPP is that, unlike *N*-cyclohexyl-*N'*-phenyl-*p*-phenylenediamine, it does not react with isocyanates and, therefore, is not incorporated into the polymer network. Thus, TPP may act as a stabilizer for the cured propellant system, preventing oxidation and subsequent degradation of physical properties.

Experiments were conducted to determine both the effective range of concentration of TPP and other phosphine equivalents of TPP. All triaryl phosphines tested were as effective as TPP in preventing reactivity increases of Poly bd R-45M resin aged at 135°F. Diaryl alkyl phosphines were somewhat less effective and aryl dialkyl and trialkyl phosphines were ineffective at preventing increases. A concentration of 0.5% appears to be the minimum amount of TPP required to effectively stabilize Poly bd R-45M resin.

CONCLUSION

Triphenylphosphine has been identified as an effective stabilizer against reactivity increases observed with Poly bd R-45M resin upon prolonged storage at ambient temperatures. Other triarylphosphines also appear to be effective stabilizers. These phosphines apparently act as acid scavengers and as antioxidants, preventing the formation of active oxygen species, whose decomposition over a period of time leads to increased reactivity of Poly bd R-45M resin with isocyanates.

135°F Aging Time (months)	Blank				2,2'-methylene- bis-(4-methyl-6- t-butyl phenol)				N-cyclohexyl- N'-phenyl-p- phenylenediamine				Phenyl didecyl phosphite				Phenyl didecyl phosphite + 2,2'- methylenebis- (4-methyl-6-t- butyl phenol)				Triphenyl- phosphine				Triphenyl- phosphine				N-cyclohexyl- N'-phenyl-p- phenylene- diamine			
	gel time	viscosity (min)	(cps, 25°C)	(min)	gel time	viscosity (min)	(cps, 25°C)	(min)	gel time	viscosity (min)	(cps, 25°C)	(min)	gel time	viscosity (min)	(cps, 25°C)	(min)	gel time	viscosity (min)	(cps, 25°C)	(min)	gel time	viscosity (min)	(cps, 25°C)	(min)	gel time	viscosity (min)	(cps, 25°C)	(min)	gel time	viscosity (min)	(cps, 25°C)	(min)
0	115	5496	119	6055	119	6134	81	6193	81	6193	81	6193	81	6193	81	5996	83	5996	81	5996	81	5996	81	5996	83	5996	81	5996	81	6134		
1	76	6193	91	6095	103	6134	68	-	75	7373	79	7373	89	5898	94	-	85	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
2	74	6289	82	5628	100	6628	55	6684	65	8257	71	8257	90	6095	95	5701	74	6134														
3	-	-	79	6387	93	6148	53	7008	47	9535	63	8945	90	6331	94	6016	83	6311														
4	49	6427	74	6128	83	6193	52	7373	42	8945	58	8945	90	6193	94	6045	82	6331														
5							48	7176																								

1. All samples were stored in an air-circulating oven at 135°F (57°C).

2. All solutions were prepared with 1% by weight antioxidant.

Table I.
Poly bdp R-43M Resin Accelerated Aging Study

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